Substituent Effect on Electronic Transition Energy of Dichlorobenzyl Radicals

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Vibronically excited but jet-cooled dichlorobenzyl radicals were generated by the corona discharge of dichlorotoluenes in a technique of corona excited supersonic expansion (CESE) using a pinhole-type glass nozzle developed in this laboratory, from which vibronic emission spectra were observed using a long-path double monochromator in the visible region. Although the spectra show very weak intensity due to the existence of Cl atoms in the precursor molecules, we could clearly identify the origin band and several well-known vibrational modes from the analysis of the spectra observed.[1] In addition, we found that the origin bands of the dichlorobenzyl radicals in the $D_1 \rightarrow D_0$ transition, as listed in Table 1, exhibit the shift to red region compared to the parental benzyl radical at 22002 cm^{-1}, suggesting the lowering energy of the excited electronic state by substitution of Cl atoms into benzene ring. The shifts of the origin bands of bi-substituted benzyl radicals are expected to be larger than those of mono-substituted ones due to the further increase of the space available for delocalized π electrons on the benzene ring and are qualitatively predictable by simply summing up the contribution of each substituent already determined from chlorobenzyl radicals. Recently, we discovered that the substituent effect on the electronic transition energy of the substituted benzyl radicals is associated with the symmetry of electronic states as well as the orientation of substituents on the benzene ring plane at given electronic states.

Table 1: Observed data of dichlorobenzyl radicals

Cl positions	Origin band (cm^{-1})	Shift (cm^{-1})
2,6-	20153	1849
3,5-	n/a	n/a
2,3-	20434	1568
2,4-	20980	1022
2,5-	19984	2018
3,4-	21098	904

In this presentation, we describe the relevance[2] of the model developed from Hückel's molecular orbital theory to explain the substituent effect on electronic transition energy as well as the spectroscopic observation of jet-cooled dichlorobenzyl radicals using a pinhole-type glass nozzle coupled with the technique of CESE.

1. Y. W. Yoon, C. S. Huh, S. K. Lee, *Chem. Phys. Lett,* **550**, 58 (2012).
2. C. S. Huh, Y. W. Yoon, S. K. Lee, *J. Chem. Phys.* **136**, 174306 (2012).